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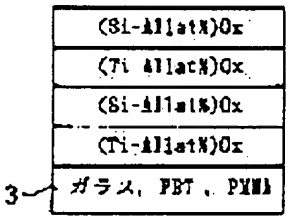
(54) THIN ANITIREFLECTION MULTILATER COATING FILM, FORMATION OF THE SAME COATING FILM AND FILM FORMING DEVICE THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To produce dense antirefrection multilayer coating film having abrasion hardness sufficient on a practical level, to provide a method for producing the same antirefrection multilayer coating film and to provide a method therefor.

SOLUTION: In a thin antireflection multilayer coating film in which thin coating films of materials having different refractive indexes are laminated into plural layers, at leat one layer among this multi-layered thin coating films is formed with a thin coating film in which ≥ two kinds of oxides of elements among Ti, Si, Al, Ta, Mg and Zr are mixed. The thin multilayer coating film is formed by a DC magnetron sputtering method using an alloy tartet in which ≥two kinds of elements among Ti, Si, Al, Ta, Mg and Zr are mixed as a target, and furthermore, a gas cong. oxygen as a reactive gas. The dense antirefrection multilayer coating film high in abrasion hardness and good in transmissivity can be obtd., and by changing the mixing ratio, the antirefrection multilayer



coating film in which the color development properties of the coating can freely be changed and accidental scratches are hardly formed can be obtd.

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グガスを成膜チャンバー内へ導入すると共に該基板上に各ターゲットの材料の薄膜を多層に形成する装置に於いて、該ターゲットのうちの少なくとも1つをTi、Si、Al、Ta、Mg、Zrのいずれかの元素を2種以上混合した合金ターゲットとすることにより、該反射防止多層膜を1個の装置で成膜できる。

【0013】

【作用】複数のTi、Si、Al、Ta、Mg、Zr等のターゲットをDCマグネトロンスパッタしてその前方を移動する基板へ多層の薄膜を成膜し、その際、O_2 ガスを導入することで該基板には各ターゲット材料の酸化物の多層膜が形成されるが、該ターゲットの少なくとも1つにTi、Si、Al、Ta、Mg、Zrのいずれかの元素を2種以上混合した合金ターゲット、例えばTi－Alのターゲットを使用して該合金組成の酸化物の膜を成膜することにより、格子欠陥が酸化物により補われ構造的に非常に緻密で硬く擦傷硬度の大きい多層膜が得られる。また、該合金組成の酸化物の膜の屈折率は、各組成の酸化物の化学量論組成の屈折率の間をその組成比率に比例してほぼ直線的に変化するので、その組成比を変化させて任意の屈折率の薄膜が得られ、膜の発色性を自在に調節できる。

【0014】

【発明の実施の形態】本発明の実施例を図面に基づき説明すると、図4は本発明の反射防止多層膜を成膜する装置の1例を示し、同図に於いて符号1は仕込み・取出しチャンバーで、その内部のトレイ2にガラスやPET或いはPMMA等のシートの基板3が設置される。該トレイ2は、開閉自在の仕切バルブ4を介して成膜チャンバー5へ正逆回転するローラー等の適当な搬送手段6により搬送される。該成膜チャンバー5内にはDCマグネトロンスパッタを行うために直流電源7へ異常放電防止用パルスユニット8を介して成膜層数に応じた例えば4基のマグネトロンカソード9が設けられ、各カソード9に＊

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＊Ti、Si、Al、Ta、Mg、Zrのいずれかの元素から成るターゲット10を取付け、これらの少なくとも1つのターゲット10をこれらの元素を2種以上混入した合金ターゲットとした。図示の例は、4個のターゲット10を全てAl合金ターゲットとしたもので、ターゲット10a、10cを$Ti-Al_{1at\%}$の合金とし、ターゲット10b、10dを$Si-Al_{1at\%}$の合金とした。11は酸素ガス等の反応性ガスを導入するガス導入系、12はArガスのスパッタガスを導入するガス導入系、13は真空ポンプに接続された排気口である。カソード9は公知の構造を有し、板面にターゲット10をボンディング等により取付け、その背面に設けた永久磁石等の磁石により該ターゲット10のスパッタ面上にマグネトロン放電用の磁界が形成される。

【0015】該成膜チャンバー5内を10^{-5}Torr台にまで排気し、スパッタリングガスArと反応性ガスO_2 を所定流量流してガス圧力を10^{-3}Torr台に維持し、電源7を通電して該成膜チャンバー5内のカソード9にマグネトロン放電を発生させる。そしてトレイ2による搬送で基板3が各ターゲット10上を通過するとき、該基板3上に各ターゲット10の材料の酸化薄膜が1層ずつ成膜され、通過し終わると、該基板3上に多層の反射防止膜が形成される。該カソード9に投入されるスパッタ電力の大きさと、基板3の搬送速度を調節することで、該酸化薄膜の膜厚を設計膜厚とすることができる。該基板3をソーダガラスとし、ターゲット9が上記組成であるとき、該成膜装置を次表2の諸元の成膜条件で成膜すると、基板3上に、（$Ti-Al_{1at\%}$）O_x 膜、（$Si-Al_{1at\%}$）O_x 膜、（$Ti-Al_{1at\%}$）O_x 膜、（$Si-Al_{1at\%}$）O_x 膜、が、夫々120Å、360Å、150Å、910Åの厚さで積層した図5に示す4層構造の反射防止多層薄膜が得られる。

【0016】

【表2】

ターゲットサイズ	5″×40″
放電モード	DCマグネトロンスパッタ(20kHz 5μmパルス型巻)
基板サイズ	500mm×850mm
Ar流量	1000SCCM
O_2 流量	240 SCCM
Ti-Al カソード 10a パワー	5 kW
Ti-Al カソード 10b パワー	20 kW
Si-Al カソード 10c パワー	2 kW
Si-Al カソード 10d パワー	10 kW
トレイスピード	500 mm/min

【0017】図5の反射防止多層薄膜の反射率特性および透過率特性を調べたところ、図6および図7の結果となった。これによれば、450nm～550nmの可視域で※

※反射率0．1%以下、透過率94%以上を示し、良好な反射防止特性が得られていることが分かる。また、その擦傷硬度は、図8の点Aで示したように、1500g/cm

^{2} を示し、点Gで示した前記従来の反射防止多層薄膜の擦傷硬度の約3倍の硬度が得られた。

【0018】また、図5の膜の第1層目のみをITO膜とし、或いは図5の第1層目乃至第4層目のいずれか1層以外をTiO、SiOとして反射防止多層薄膜を成膜したが、これらの場合の擦傷硬度は、図8の点B～Fで示したように、1000g/cm^2 の荷重硬度となり、従来の反射防止多層薄膜よりも十分な硬度が得られた。

【0019】Ti、Si、Al、Ta、Mg、Zrのいずれかの2種以上の元素からなる合金ターゲットを出発材料としてAr＋O_2 ガスを導入しながら反応性DCスパッタにより成膜した2元素以上の酸化物は、各々の金属元素の酸化物の格子定数が異なるため、格子欠陥を互いの酸化物が補い、構造的に緻密で非常に硬い膜であることが見出された。1例としてTiに、Si、Al、Ta、Mg、Zrを比率を変えて混入した膜の擦傷硬度を、図9に示した。これによれば、$Ti_{1at\%}$ 乃至 $Ti_{93at\%}$ の範囲で混合した場合の擦傷硬度は、1500g/cm^2 以上の荷重を加えても擦傷痕が発生せず、従来の単元素の酸化物の膜よりも約3倍の硬度を持つことが分かる。また、この1例の膜の屈折率は、図10に示したように、夫々の化学量論組成の酸化物が有する屈折率の間を組成比率に比例してほぼ直線的に変化し、1at%程度のTi混入量では、屈折率の変化がわずかであり、例えば、$Ti-Si_{1at\%}$ の酸化物では、屈折率の変化がTiO_2 の2.6からわずか－0.0115変化するだけで、膜設計上何等問題が生じることがない。さらに、組成比を変化させることによって、任意の屈折率を有する酸化物膜が得られ、また膜の発色の自在性があるので、膜設計上大きな利点となる。

【0020】以上の傾向は、前記の元素の組合わせ以外の組合わせにおいても、全く同様の結果が見られた。

【0021】尚、本発明では、2元素のターゲット材を酸素ガスにより酸化物の膜を成膜したが、SiONのように可視域で94%以上の透過率をもつものであれば、反応性ガスとしてO_2 の一部をN_2 、N_2O、NH_3 等の窒化系ガスで置換し、酸化物と窒化物の混合物としても、2元素酸化物と同様の効果を発揮させることができる。また、O_2 の一部をCO_2 、CO、CF_4 、CH_4 等、カーボンを含んだガスで置換してもよい。

【0022】また、図4の基板の仕込みと取出しを共通のチャンバーとしたインターバック形式の成膜装置を、仕込みチャンバーと取出しチャンバーを個別に備える3室以上のチャンバー構成のインライン形式の装置としてもよい。さらに、PET、PMMA等の長尺巻物状の基板に成膜を行うロールコーター形式のスパッタ装置、或いは枚葉装置として用いられるマルチチャンバー形式のスパッタ装置も適用可能である。

【0023】

【実施例】図4に示す装置において、500mm×850mmのソーダガラスの基板を仕込み・取出しチャンバー内のトレイに用意し、成膜チャンバー内を10^{-5}Torrに排気したのち、ガス導入系からArガスを1000SCCMとO_2 ガスを240SCCM流し、ガス圧を10^{-3}Torr台に維持しながら、該成膜チャンバー内の各マグネトロンカソードに直流電源から通電した。各カソードは5インチ×40インチの寸法の各ターゲットが設けられており、ターゲット10a、10cは$Ti-Al_{1at\%}$、ターゲット10b、10dは$Si-Al_{1at\%}$で、ターゲット10aには電源から5Kwを投入し、10bには2Kw、10cには20Kw、10dには10Kwを夫々投入し、トレイを500mm/minの速度で移動させて基板上に図5に示す4層の反射防止多層膜をDCマグネトロンスパッタで成膜した。第1層の$(Ti-Al_{1at\%})O_x$ 膜の膜厚は120Å、第2層の$(Si-Al_{1at\%})O_x$ 膜の膜厚は360Å、第3層の$(Ti-Al_{1at\%})O_x$ 膜の膜厚は1150Å、第4層の$(Si-Al_{1at\%})O_x$ 膜の膜厚は910Åであった。

【0024】この多層膜の擦傷硬度を、前記のように0番のスチールウール1cm^2 あたりに定荷重を加え、2cm/secの引っかき速度で膜表面を5回ランビングしたのち、肉眼にて1cm幅当たりに1本以上の擦傷痕を生じるときの最低荷重で測定したところ、1500g/cm^2 であった。またその反射率と透過率は450nm～550nmの可視域で夫々0.1%以下と94%以上で、良好な反射防止特性が得られた。

【0025】

【発明の効果】以上のように、本発明によるときは、多層薄膜の反射防止膜を構成する多層薄膜のうちの少なくとも1層の薄膜をTi、Si、Al、Ta、Mg、Zrのいずれかの元素の酸化物が2種以上混入している薄膜としたので、緻密で擦傷硬度が高く透過率の良い射防止多層薄膜が得られ、その混入比を変更することで膜の発色性も自在に変更でき、不慮の引っ掻き傷が付きにくい反射防止多層膜が得られる効果があり、また本発明の方法と装置によれば、導電性のある合金ターゲットを用いるため、反応性DCスパッタリングが採用でき、高速で低温成膜が可能となり、反射防止多層薄膜の生産性が向上する等の効果がある。

【図面の簡単な説明】

【図1】従来の反射防止多層薄膜の構成の模式図

【図2】従来の反射防止多層薄膜の成膜装置の概略的側面図

【図3】従来の反射防止多層薄膜の単層膜の擦傷硬度図

【図4】本発明の反射防止多層薄膜の成膜装置の実施例の概略的側面図

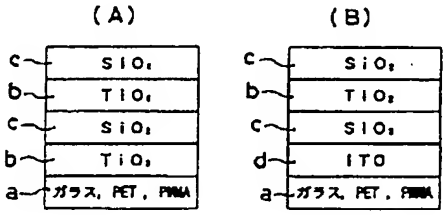
【図5】本発明の反射防止多層薄膜の構成の模式図

【図6】図5に示した反射防止多層薄膜の反射率特性曲線図

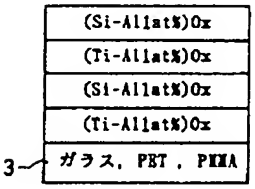
【図7】図5に示した反射防止多層薄膜の透過率特性曲

線図
【図８】本発明の反射防止多層薄膜の擦傷硬度図
【図９】混入比を変化させた本発明の反射防止多層薄膜の擦傷硬度図
【図１０】混入比を変化させた本発明の反射防止多層薄膜の屈折率の線図
【符号の説明】
３　基板　　５　成膜チャンバー
６　基板搬送手段　　７　直流電源
９　マグネトロンカソード
１０、１０ａ、１０ｂ、１０ｃ、１０ｄ　合金ターゲット
１１、１２　ガス導入系

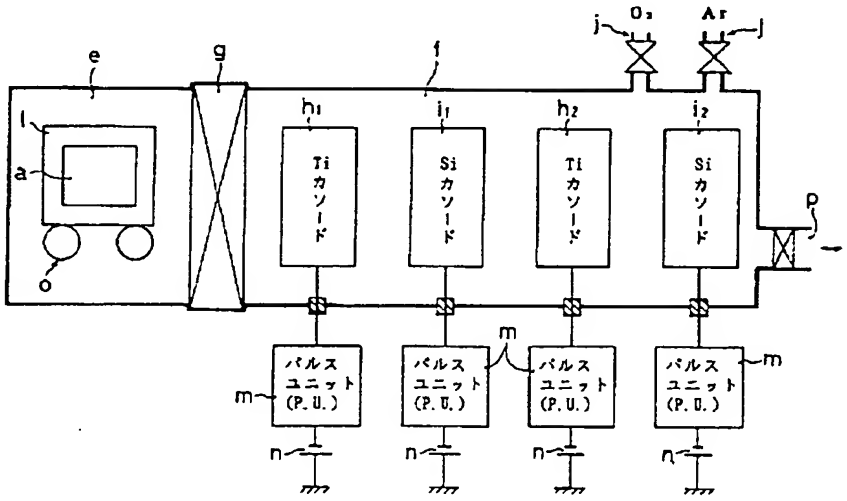
【図１】



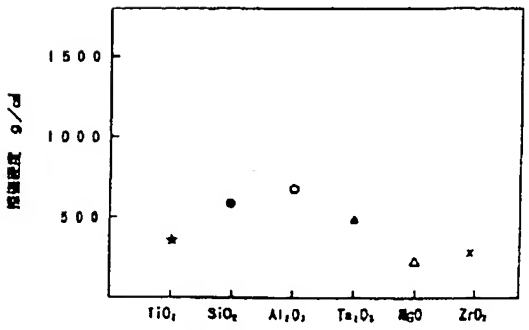
【図５】



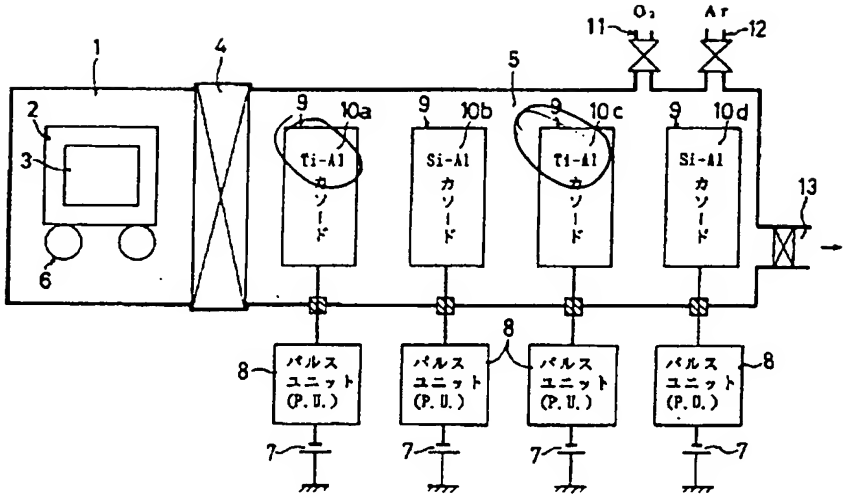
【図２】



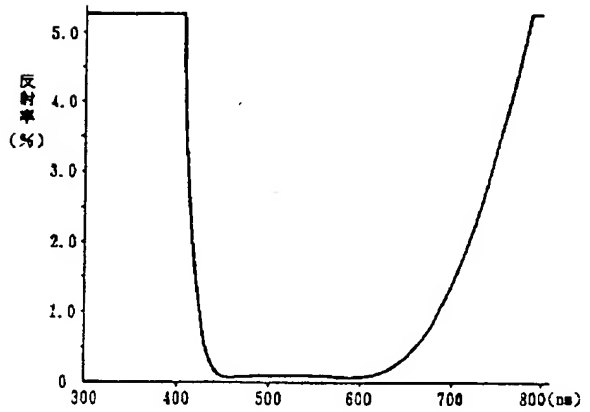
【図３】



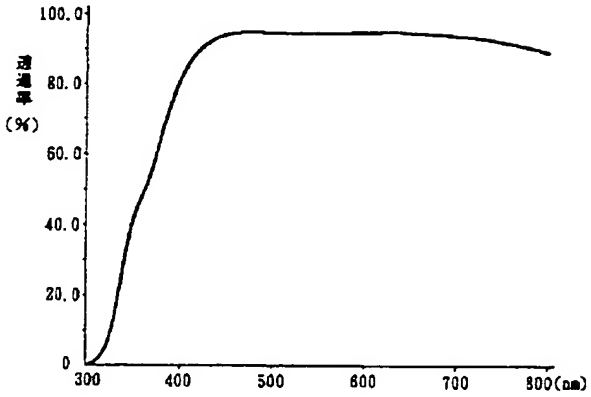
【図4】


O₂
Ar
11
12
1
4
5
2
3
6
9
10a
10b
10c
10d
Ti-Al カソード
Si-Al カソード
13
8
パルスユニット (P.U.)
7

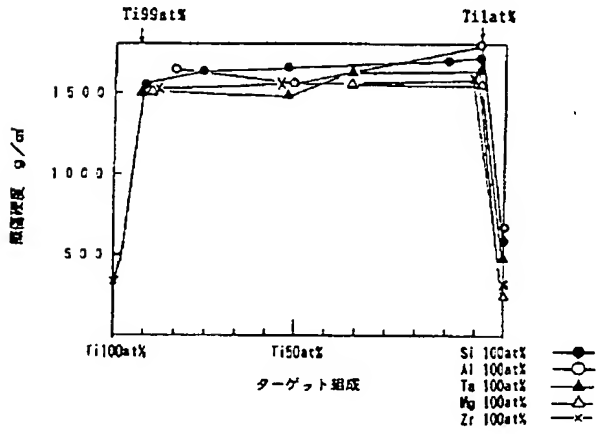
【図6】


5.0
4.0
3.0
2.0
1.0
0
(%)
300
400
500
600
700
800(nm)

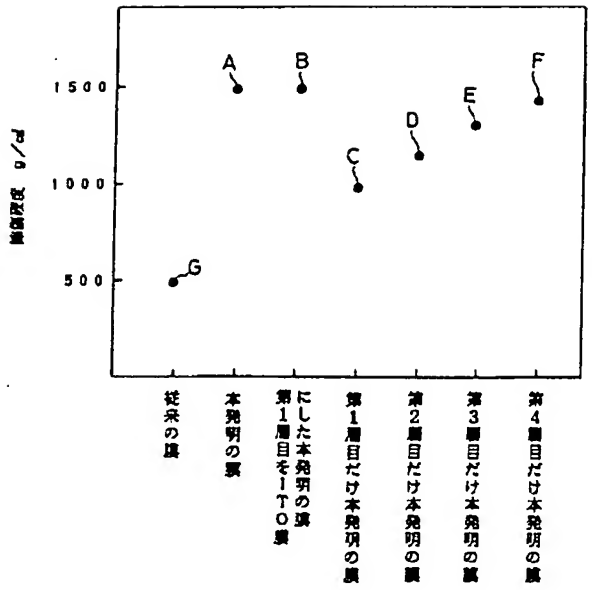
【図7】


100.0
80.0
60.0
40.0
20.0
0
(%)
300
400
500
600
700
800(nm)

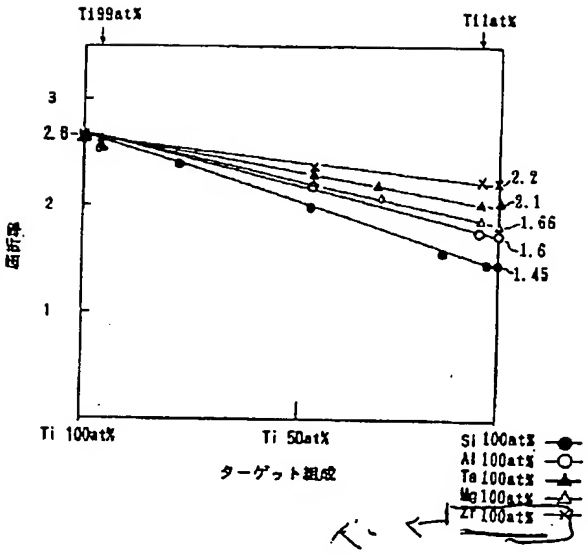
【図9】


Ti99at%
Ti1at%
1500
1000
500
Ti100at%
Ti50at%
ターゲット組成
Si 100at%
Al 100at%
Ta 100at%
Mg 100at%
Zr 100at%

【図8】



【図10】



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] The invention in this application relates to the acid-resisting multilayer applied to optical instruments and parts, such as a spectacle lens, its membrane formation method, and its membrane formation equipment.
[0002]
[Description of the Prior Art] Conventionally, while forming the dielectric materials of a low refractive index and a high refractive index by turns on both sides or one side of a spectacle lens and preventing the fall of the visibility by reflection in the inside of a lens, preventing reflection of light is performed on the outside. Moreover, recently, what formed the antireflection film and installed this on the display at ****** or the front face on the macromolecule substrate of the shape of a film, such as a display, PET (polyethylene terephthalate), PMMA (polymethylmethacrylate), etc. which the outdoor daylight in VDT work was reflected and formed the direct antireflection film on the front face for lump prevention, is marketed.
[0003] Membrane formation of the antireflection film to a spectacle lens considers as the start material of membrane formation of SiO2, TiO2, MgF, etc., and membrane formation is performed by the electron-beam-evaporation method. moreover, the method of making a front face into irregularity and reducing the surface reflected light by etching processing by fluoric acid etc. in giving the function of acid resisting to big screens, such as a display, and a screen -- after a spray application -- printing -- coming out -- SiO2 etc. -- the method of forming an antireflection film is also enforced
[0004] However, recently, since the thickness control at the time of membrane formation is easy, the sputtering method with a sufficient controllability which can form membranes attracts attention in the high-definition antireflection film from the large area. Also in the sputtering method, the reactant DC magnetron-sputtering method for the ability to realize low-temperature membrane formation at high speed is occupying the mainstream on a process from a viewpoint on the processes run that membrane formation is possible, at low temperature also at the viewpoint of productivity, and a film top.
[0005] As the composition of the multilayer of the conventional antireflection film is shown in (A) of drawing 1 , and (B), each class of (A) of drawing 1 is the oxide of a single element, and it is TiO2 of a high refractive index [top / transparent substrates a /, such as glass, and PET, PMMA,]. The membranous layer b and SiO2 of a low refractive index The laminating of the membranous layer c is carried out to four layers by the thickness which balanced the design value by turns. moreover, the thing for which the 1st layer d on the transparent substrate a is an ITO film, the laminating of the layers b and c of the high refractive index as the case of (A) with other three same layers and a low refractive index was carried out by turns, and the multilayer of (B) of drawing 1 gives conductivity to the 1st layer d -- electromagnetism -- a shield is made to have
[0006] As [show / one example of the composition of the equipment which forms such a multilayer / moreover, / in drawing 2] It has the two-room composition which preparation and the drawing chamber e, and the membrane formation chamber f divided, and was connected through Bulb g. in this membrane

formation chamber f The cathodes h1 and h2 which prepared the target for forming high refractive-index films, such as Ti The cathode i1 and i2 which prepared the target for membrane formation of low refractive-index films, such as B or Si of which P dope was done, are stationed by turns, and it is Ar gas and O2 from gas feed systems j and j during membrane formation. Gas is introduced, respectively and an oxide film is formed in the transparent substrate a by reactant membrane formation. Substrate a is conveyed by the substrate conveyance meanses o, such as a roll by which the roll control was attached and carried out to Tray l. In addition, DC power supply n are connected to each cathode h and i through the pulse generating unit m for controlling the unusual electric discharge at the time of performing DC sputtering. p is the exhaust air system connected to the vacuum pump.

[0007] When forming an acid-resisting multilayer to Substrate a with the equipment of drawing 2 , in preparation and the drawing chamber e Glass, The substrate a of the shape of a sheet, such as PET or PMMA, is attached in Tray l. Sputtering gas Ar and reactant gas O2 after exhausting Substrate a to a 10-5Torr base by the exhaust air system p beforehand with this tray l through the partition bulb g with the conveyance means o It conveys into the membrane formation chamber f which carried out the predetermined flow rate style and maintained gas pressure on the 10-3Torr base. And when energize to each cathodes h and i from a power supply n, they are made to generate spatter electric discharge and Substrate a passes through the front of each cathodes h and i, the oxide film of the design thickness corresponding to the electric discharge power and the substrate bearer rate of each cathode is formed like drawing 1 on Substrate a at a multilayer, and it is **. The item of the membrane formation conditions in this case was shown in Table 1.

[0008]

[Table 1]

ターゲットサイズ	5″ × 4 0″
放電モード	ＤＣマグネトロンスパッタ(20kHz 5μmパルス重畳)
基板サイズ	５００mm×８５０mm
Ａｒ流量	１０００SCCM
O_2 流量	２４０ SCCM
Tiカソード h_1 パワー	５ kW
Tiカソード h_2 パワー	２０ kW
Siカソード i_1 パワー	２ kW
Siカソード i_2 パワー	１０ kW
トレイスピード	５００ mm／min

[0009]

[Problem(s) to be Solved by the Invention] In order that direct ** of the antireflection film may be carried out at outdoor daylight and it may usually touch impurities, such as people's hand and dust of the external world, the maintenance work of wiping off the dirt periodically is required. If a keen thing touches the time of the wiping work, and unexpected in such a case, a blemish will occur on a film, and the acid-resisting function of film original will be spoiled. Each class of the conventional antireflection film is 500 g/cm2. There is only an abrasion degree of hardness of a grade and there was a fault with inadequate intensity practically. Each monolayer TiO2 which constitutes the conventional antireflection film, SiO2, aluminum 2O3, Ta 2O5, MgO, and ZrO2 The abrasion degree of hardness was shown in drawing 3 . An abrasion degree of hardness is steel wool 1cm2 of No. 0. After adding constant stress to a hit and acting as Laon Byng of the film front face 5 times at the scratch speed of 2 cm/sec, the minimum load when producing one or more abrasion marks per 1cm width of face expresses with the naked eye.

[0010] Moreover, it is Ar and O2, using charges of a unit material, such as Ti, Si, aluminum, Ta, Mg,

and Zr, as start material by the reactant DC sputtering method conventionally. If a spatter is performed introducing gas TiO2 which formed membranes, SiO2, Ta 2O5, MgO, and ZrO2 etc. -- since the oxide of a single element includes many lattice defects in a film in process of oxide generation, a film is structurally weak and the bird clapper is known Therefore, it also has the fault that density is coarse and the antireflection film which formed membranes by the reactant DC sputtering method is weak.
[0011] this invention aims at offering the method and equipment which manufacture offering the precise antireflection film which has sufficient abrasion degree of hardness on practical use level, and this antireflection film.
[0012]
[Means for Solving the Problem] In this invention, the precise antireflection film which has sufficient abrasion degree of hardness was obtained in the antireflection film of the multilayered film in which the thin film of the material from which the refractive index differed on the substrate carried out the laminating to two or more layers by making the thin film of at least one layer of these multilayered films into the thin film which two or more sorts of oxides of the element of Ti, Si, aluminum, Ta, Mg, or Zr are mixing. This acid-resisting multilayer, introducing reactant gas and sputtering gas simultaneously in a membrane formation chamber The spatter of the target which consists of the element of Ti, Si, aluminum, Ta, Mg, or Zr is carried out by the DC magnetron-sputtering method. In the method of forming the antireflection film of a multilayered film by carrying out the laminating of the thin film of the material from which the refractive index differed on the substrate which moves in the front of this target one by one The thin film of at least one layer of this multilayered film as this target Ti, Si, While using the alloy target in which two or more sorts of elements of aluminum, Ta, Mg, or Zr were made to mix, it can manufacture by the method of forming membranes to the thin film which two or more sorts of oxides of the element of Ti, Si, aluminum, Ta, Mg, or Zr mixed using the gas which contains oxygen as reactant gas. Moreover, the membrane formation chamber equipped with the exhaust air system and two or more DC sputtering cathodes arranged in this membrane formation chamber, The target prepared in each cathode, and a substrate conveyance means to pass the front of each target for a substrate, It is membrane formation equipment which consists of the gas feed system into which reactant gas and sputtering gas are introduced into this membrane formation chamber. In the equipment which forms the thin film of the material of each target on this substrate at a multilayer while introducing reactant gas and sputtering gas into a membrane formation chamber from this gas feed system This acid-resisting multilayer can be formed with one equipment by using at least one of these targets as the alloy target which mixed two or more sorts of elements of Ti, Si, aluminum, Ta, Mg, or Zr.
[0013]
[Function] A multilayer thin film is formed to the substrate which carries out DC magnetron sputtering of two or more targets, such as Ti, Si, aluminum, Ta, Mg, and Zr, and moves in the front, and it is O2 in that case. Although the multilayer of the oxide of each target material is formed in this substrate by introducing gas By forming the film of the oxide of this alloy composition to at least one of the targets of these using the alloy target which mixed two or more sorts of elements of Ti, Si, aluminum, Ta, Mg, or Zr, for example, the target of Ti-aluminum A lattice defect is compensated with an oxide and a structural very precise and hard multilayer with a large abrasion degree of hardness is obtained. Moreover, since the refractive index of the film of the oxide of this alloy composition changes almost linearly between the refractive indexes of the stoichiometric composition of the oxide of each composition in proportion to the composition ratio, the composition ratio is changed, the thin film of arbitrary refractive indexes is obtained, and it can adjust membranous coloring nature free.
[0014]
[Embodiments of the Invention] If the example of this invention is explained based on a drawing, drawing 4 shows one example of the equipment which forms the acid-resisting multilayer of this invention, in this drawing, signs 1 will be preparation and a drawing chamber, and the substrate 3 of sheets, such as glass, and PET or PMMA, will be installed in the tray 2 of the interior. It is conveyed by the suitable conveyance meanses 6, such as a roller which right-rotates reversely to the membrane formation chamber 5 through the batch bulb 4 which can open and close this tray 2 freely. In order to

perform DC magnetron sputtering in this membrane formation chamber 5, through the pulse unit 8 for unusual electric discharge prevention, four sets of the magnetron cathodes 9 were prepared, for example, the target 10 according to the membrane formation number of layers which changes from the element of Ti, Si, aluminum, Ta, Mg, or Zr to each cathode 9 was attached in DC power supply 7, and these at least one target 10 was used as the alloy target which mixed two or more sorts of these elements. The example of illustration was what used four targets 10 as aluminum alloy target altogether, used Targets 10a and 10c as the Ti-aluminum1at% alloy, and used Targets 10b and 10d as the Si-aluminum1at% alloy. The gas feed system into which 11 introduces reactant gas, such as oxygen gas, the gas feed system into which 12 introduces the spatter gas of Ar gas, and 13 are the exhaust ports connected to the vacuum pump. A cathode 9 has well-known structure, a target 10 is attached in a plate surface with bonding etc., and the magnetic field for magnetron discharges is formed on the spatter side of this target 10 with magnets, such as a permanent magnet prepared in the tooth back.

[0015] The inside of this membrane formation chamber 5 is exhausted even on a 10-5Torr base, and they are sputtering gas Ar and reactant gas O2. A predetermined flow rate style is carried out, gas pressure is maintained on a 10-3Torr base, a power supply 7 is energized, and the cathode 9 in this membrane formation chamber 5 is made to generate a magnetron discharge. And if membranes are formed one layer at a time on this substrate 3 and the oxidization thin film of the material of each target 10 finishes passing to it when a substrate 3 passes through each target 10 top by conveyance on a tray 2, a multilayer antireflection film will be formed on this substrate 3. Let thickness of this oxidization thin film be design thickness by adjusting the size of the spatter power supplied to this cathode 9, and the bearer rate of a substrate 3. When this substrate 3 is made into a soda glass and a target 9 is the above-mentioned composition, If this membrane formation equipment is formed on the membrane formation conditions of the item of following ** 2, it is OX (Ti-aluminum1at%) on a substrate 3. Film, (Si-aluminum1at%) OX A film and OX (Ti-aluminum1at%) A film and OX (Si-aluminum1at%) The acid-resisting multilayered film of four layer structures shown in drawing 5 in which film ** carried out the laminating by the thickness of 120A, 360A, 1150A, and 910A, respectively is obtained.

[0016]

[Table 2]

ターゲットサイズ	5″ ×40″
設定モード	DCマグネトロンスパッタ(20kHz 5μmパルス重畳)
基板サイズ	500mm×850mm
Ar流量	1000SCCM
O_2 流量	240 SCCM
Ti-Al カソード10a パワー	5 kW
Ti-Al カソード10b パワー	20 kW
Si-Al カソード10c パワー	2 kW
Si-Al カソード10d パワー	10 kW
トレイスピード	500 mm/min

[0017] When the reflection factor property and permeability property of an acid-resisting multilayered film of drawing 5 were investigated, a result of drawing 6 and drawing 7 was brought. According to this, it turns out that a 450nm - 550nm visible region shows 0.1% or less of reflection factors, and 94% or more of permeability, and the good acid-resisting property is acquired. Moreover, the abrasion degree of hardness is 1500 g/cm2, as shown in respect of [A] drawing 8 . The degree of hardness of the aforementioned conventional acid-resisting multilayered film about 3 times the degree of hardness of an abrasion which was shown and was shown with Point G was obtained.

[0018] Moreover, although the acid-resisting multilayered film was formed as TiO and SiO, as the

abrasion degree of hardness in these cases showed except the 1st layer of drawing 5 , or any one layer [4th] layer by point B-F of drawing 8 by using the 1st layer of the film of drawing 5 as an ITO film, it is 1000 g/cm2. It became a load degree of hardness and sufficient degree of hardness was obtained rather than the conventional acid-resisting multilayered film.

[0019] It is Ar+O2, using as start material the alloy target which consists of two or more sorts of elements of Ti, Si, aluminum, Ta, Mg, or Zr. It was found out that a mutual oxide compensates a lattice defect, and the oxide of two or more elements which formed membranes by reactant DC spatter while introducing gas is structurally precise, and is very a stiff film since the lattice constants of the oxide of each metallic element differ. The abrasion degree of hardness of the film which changed the ratio into Ti and mixed Si, aluminum, Ta, Mg, and Zr in it as one example was shown in drawing 9 . According to this, it is Ti1at% or Ti99at%. The abrasion degree of hardness at the time of mixing in the range is 2 1500g/cm. It turns out that abrasion marks do not occur even if it adds the above load, but it has one about 3 times the degree of hardness of this rather than the film of the oxide of the conventional single element. Moreover, as the refractive index of this film of one example was shown in drawing 10 , between the refractive indexes which the oxide of each stoichiometric composition has is changed almost linearly in proportion to a composition ratio. In the about [1at%] amount of Ti mixing, change of a refractive index is slight, for example, change of a refractive index is TiO2 with an Ti-Si1at% oxide. Only by changing from 2.6 -0.0115 times only, a problem does not arise at all on a film design. Furthermore, since the oxide film which has arbitrary refractive indexes by changing a composition ratio is obtained and there is free nature of coloring of a film, it becomes a big advantage on a film design.

[0020] Also in combination other than the combination of the element of the above [the above inclination], the same result was completely seen.

[0021] in addition -- although the film of an oxide was formed for the target material of two elements by oxygen gas in this invention, if it is what has 94% or more of permeability by the visible region like SiON -- as reactant gas -- O2 a part -- N2, N2 O, and NH3 etc. -- nitriding system gas can replace and the effect same also as mixture of an oxide and a nitride as 2 element oxide can be demonstrated O2 [moreover,] a part -- CO2, CO, CF4, and CH4 etc. -- the gas containing carbon may replace

[0022] Moreover, it is good also as equipment of the inline-type formula of the chamber composition of three or more rooms which takes out the membrane formation equipment of the interchange back form which used the preparation and drawing of a substrate of drawing 4 as the common chamber with a preparation chamber, and is individually equipped with a chamber. Furthermore, the sputtering system of multi chamber form used as the sputtering system or sheet equipment of the roll-coater form which forms membranes to the substrate of the shape of a long roll, such as PET and PMMA, is also applicable.

[0023]

[Example] It is the gas feed system after preparing the substrate of a 500mmx850mm soda glass for the tray in preparation and a drawing chamber and exhausting the inside of a membrane formation chamber to 10-5Torr in the equipment shown in drawing 4 to Ar gas 1000SCCM(s) and O2 It energized from DC power supply to each magnetron cathode in this membrane formation chamber, having passed gas 240 SCCMs and maintaining gas pressure on a 10-3Torr base. As for each cathode, each target of a 5 inch x40 inch size is prepared, Targets 10a and 10c are Ti-aluminum1at%, and Targets 10b and 10d are Si-aluminum1at%. 5Kw(s) were supplied to target 10a from the power supply, 20Kw(s) were supplied to 2Kw(s) and 10c, 10Kw(s) were supplied to 10d at 10b, respectively, and the acid-resisting multilayer of four layers which is made to move a tray at the rate of 500 mm/min, and is shown on a substrate at drawing 5 was formed by DC magnetron sputtering. OX of the 1st layer (Ti-aluminum1at%) Membranous thickness is 120A and OX (Si-aluminum1at%) of the 2nd layer. Membranous thickness is 360A and OX (Ti-aluminum1at%) of the 3rd layer. Membranous thickness is 1150A and OX (Si-aluminum1at%) of the 4th layer. Membranous thickness was 910A.

[0024] the abrasion degree of hardness of this multilayer -- above -- steel wool 1cm2 of No. 0 per -- the place measured by the minimum load when producing one or more abrasion marks per 1cm width of face with the naked eye after adding constant stress and acting as Laon Byng of the film front face 5

times at the scratch speed of 2 cm/sec -- 1500 g/cm2 it was . Moreover, the reflection factor and permeability are 0.1% or less and 94% or more in a 450nm - 550nm visible region, respectively, and the good acid-resisting property was acquired.

[0025]

[Effect of the Invention] As mentioned above, since the oxide of the element of Ti, Si, aluminum, Ta, Mg, or Zr made the thin film of at least one layer of the multilayered films which constitute the antireflection film of a multilayered film the thin film currently mixed two or more sorts when based on this invention It is precise, and it shoots, a prevention multilayered film is obtained and an abrasion degree of hardness can also change membranous coloring nature free by the thing with high and sufficient permeability for which the mixing ratio is changed. In order to use the alloy target which it is effective in the acid-resisting multilayer to which an unexpected scratch cannot be attached easily being obtained, and has conductivity according to the method and equipment of this invention, Reactant DC sputtering can be adopted, low-temperature membrane formation is attained at high speed, and there is an effect of the productivity of an acid-resisting multilayered film improving.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
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CLAIMS

[Claim(s)]
[Claim 1] The acid-resisting multilayered film characterized by making the thin film of at least one layer of these multilayered films into the thin film which two or more sorts of oxides of the element of Ti, Si, aluminum, Ta, Mg, or Zr are mixing in the antireflection film of the multilayered film in which the thin film of the material from which the refractive index differed on the substrate carried out the laminating to two or more layers.
[Claim 2] It is the acid-resisting multilayered film according to claim 1 characterized by the above-mentioned substrate and the multilayered film being transparent, and the above-mentioned substrate being either of the high polymer film substrates, such as ceramic substrates, such as glass, a polyethylene terephthalate, and polymethylmethacrylate.
[Claim 3] Introducing reactant gas and sputtering gas simultaneously in a membrane formation chamber The spatter of the target which consists of the element of Ti, Si, aluminum, Ta, Mg, or Zr is carried out by the DC magnetron-sputtering method. In the method of forming the antireflection film of a multilayered film by carrying out the laminating of the thin film of the material from which the refractive index differed on the substrate which moves in the front of this target one by one The thin film of at least one layer of this multilayered film as this target Ti, Si, The gas which contains oxygen as reactant gas while using the alloy target in which two or more sorts of elements of aluminum, Ta, Mg, or Zr were made to mix is used. Ti, The membrane formation method of the acid-resisting multilayer characterized by forming membranes to the thin film which two or more sorts of oxides of the element of Si, aluminum, Ta, Mg, or Zr mixed.
[Claim 4] It is the membrane formation method of the acid-resisting multilayered film according to claim 3 characterized by the above-mentioned substrate and the multilayered film being transparent, and the above-mentioned substrate being either of the high polymer film substrates, such as ceramic substrates, such as glass, a polyethylene terephthalate, and polymethylmethacrylate.
[Claim 5] In the equipment which forms the thin film of the material of each target on this substrate at a multilayer while being membrane formation equipment characterized by providing the following and introducing reactant gas and sputtering gas into a membrane formation chamber from this gas feed system Membrane formation equipment of the acid-resisting multilayer characterized by using at least one of these targets as the alloy target which mixed two or more sorts of elements of Ti, Si, aluminum, Ta, Mg, or Zr. The membrane formation chamber equipped with the exhaust air system. Two or more DC magnetron cathodes arranged in this membrane formation chamber. The target prepared in each cathode. A substrate conveyance means to pass the front of each target for a substrate, and the gas feed system which introduces reactant gas and sputtering gas into this membrane formation chamber.

[Translation done.]